

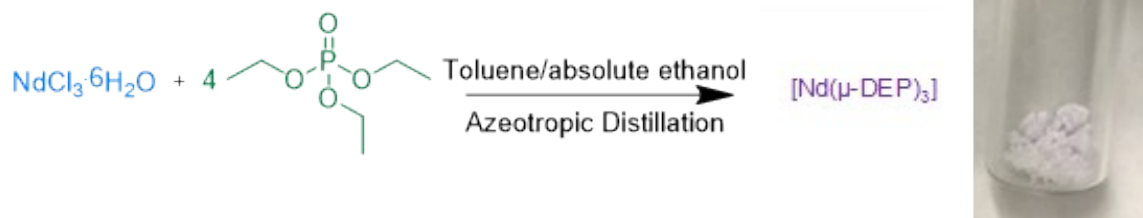
Halide-Free Neodymium Phosphate Based Catalyst for Highly *Cis*-1,4 Selective Polymerization of Dienes

Yixin Ren, Justin T. Miller, Stefanie T. Polderman, Trinh D. Vo, Adele C. M. Wallace, John Michael O. Cue, Sarah T. Tran, Michael C. Biewer, Mihaela C. Stefan*

*Department of Chemistry and Biochemistry, The University of Texas at Dallas, 800 W. Campbell Rd., Richardson, TX 75080-3021

*Department of Bioengineering, The University of Texas at Dallas, 800 W. Campbell Rd., Richardson, Texas, 75080-3021

Mihaela C. Stefan (E-mail: mci071000@utdallas.edu)



Scheme S1. Synthesis of $[\text{Nd}(\mu\text{-DEP})_3]_x$ *via* azeotropic distillation method.

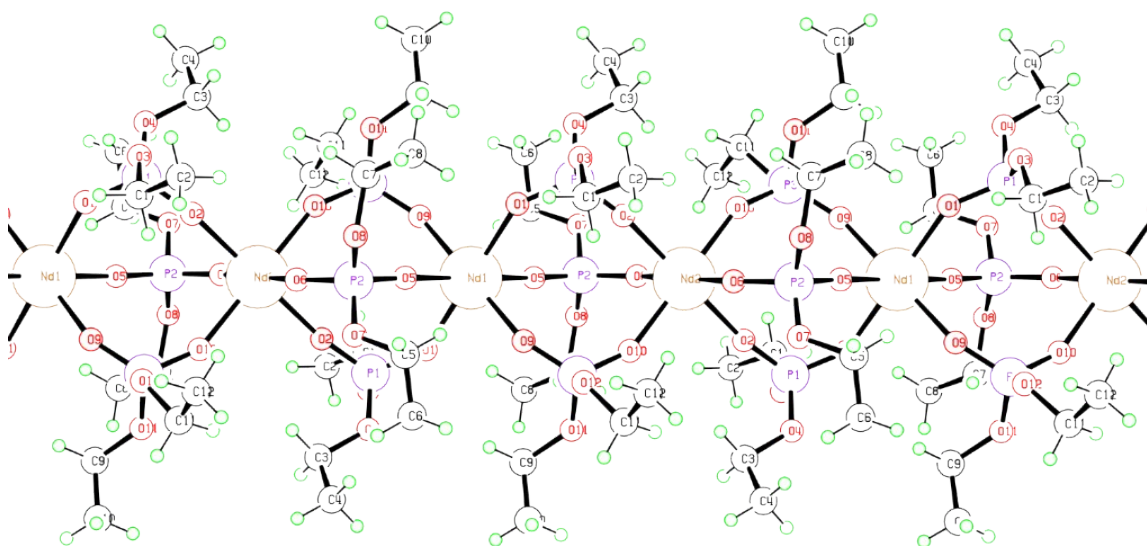


Figure S1. ORTEP diagram for $[\text{Nd}(\mu\text{-DEP})_3]_x$

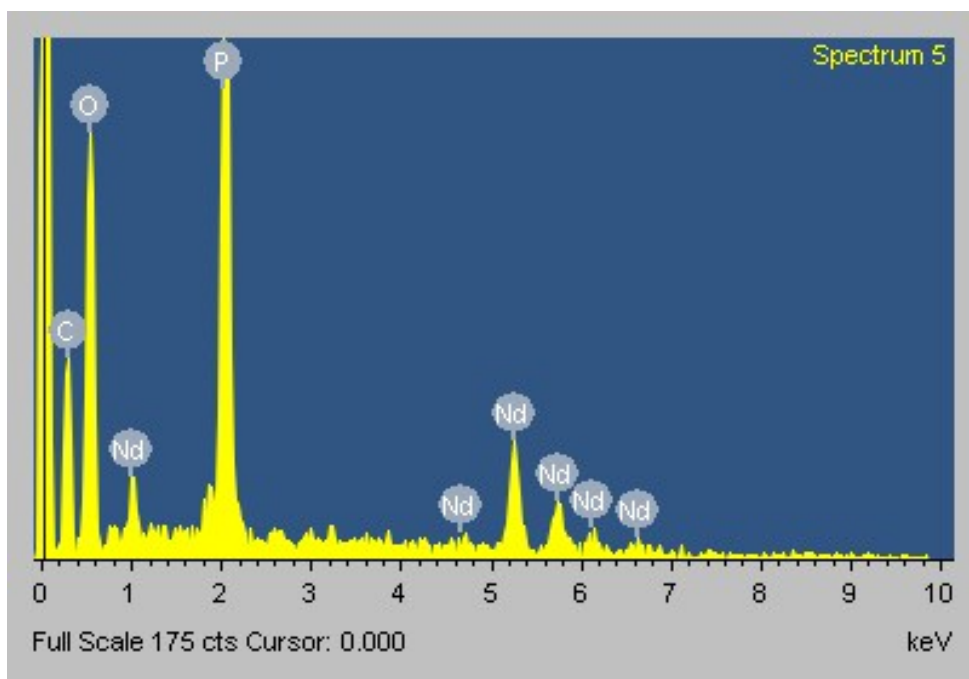


Figure S2. EDX result of $[\text{Nd}(\mu\text{-DEP})_3]_x$.

Table S1. Control experiments for the poly(β -myrcene) synthesis.

| Nd compound | [Nd]:[TIBA] | Yield (%) | M_n (g/mol) | PDI | Cis-1,4 (%) |
|---|-------------|--------------------------------|---------------|------|-------------|
| $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ | 1:0 | trace | - | - | - |
| $[\text{Nd}(\mu\text{-DEP})_3]_x$ | 1:0 | trace | - | - | - |
| TIBA | 0:1 | Insoluble cross-linked polymer | | | - |
| $[\text{Nd}(\mu\text{-DEP})_3]_x/\text{TIBA}$ | 1:30 | 100 | 13,000 | 1.80 | 96.0 |

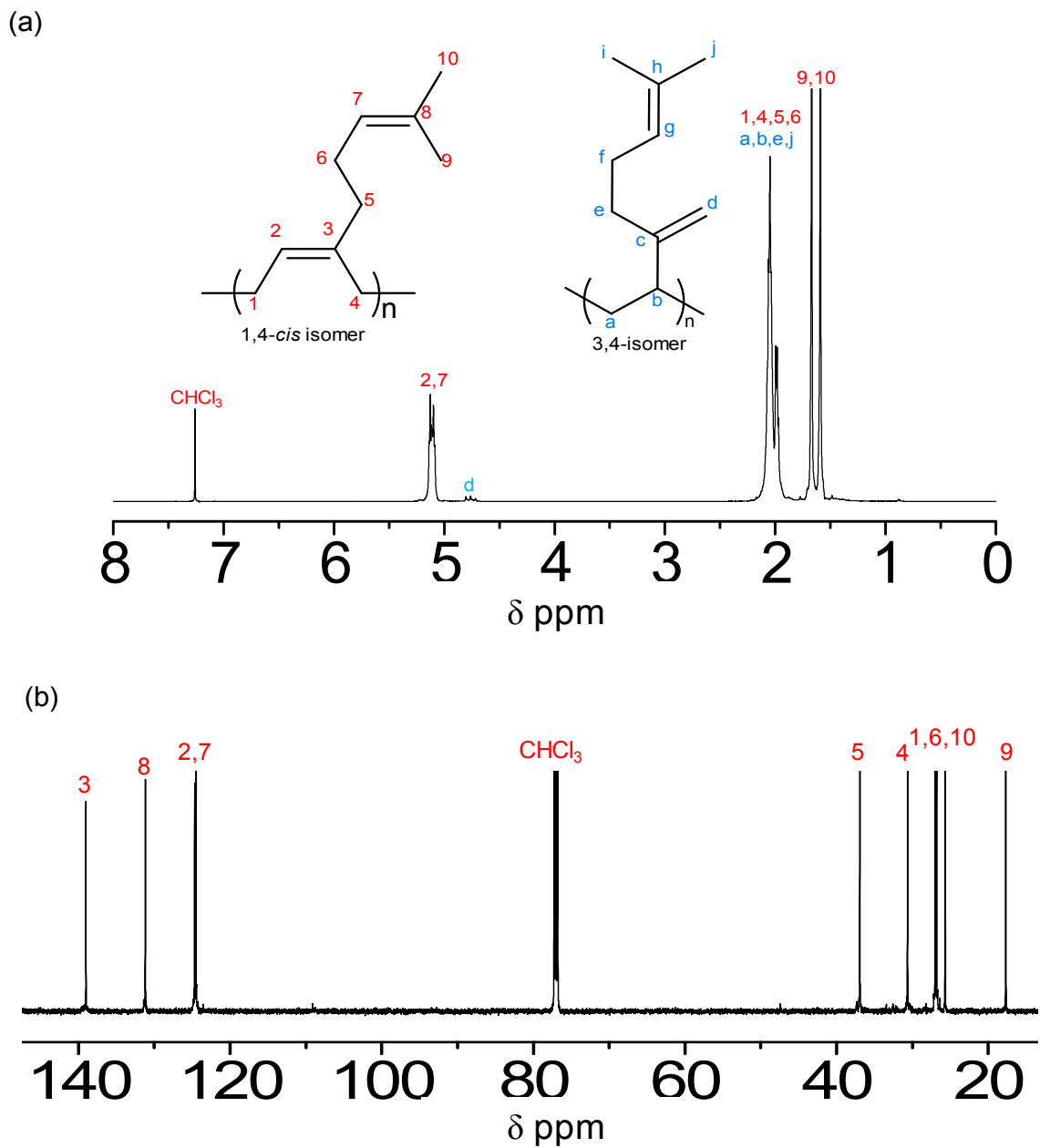


Figure S3. (a) ^1H and (b) ^{13}C NMR spectrum of the poly(β -myrcene). Reaction condition: $[\text{Nd}]:[\text{TIBA}]:[\beta\text{-myrcene}] = 1:30:250$ at room temperature for 2 hours.

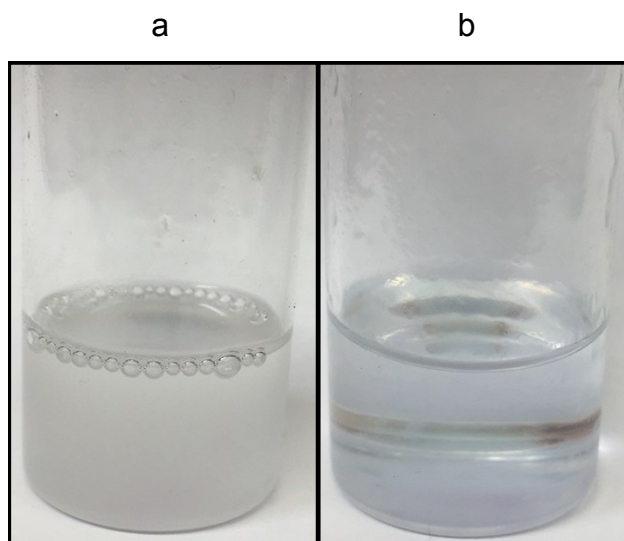


Figure S4. Solubility test before and after addition of the co-catalyst TIBA, (a) the Nd catalyst in toluene, (b) after addition of TIBA.

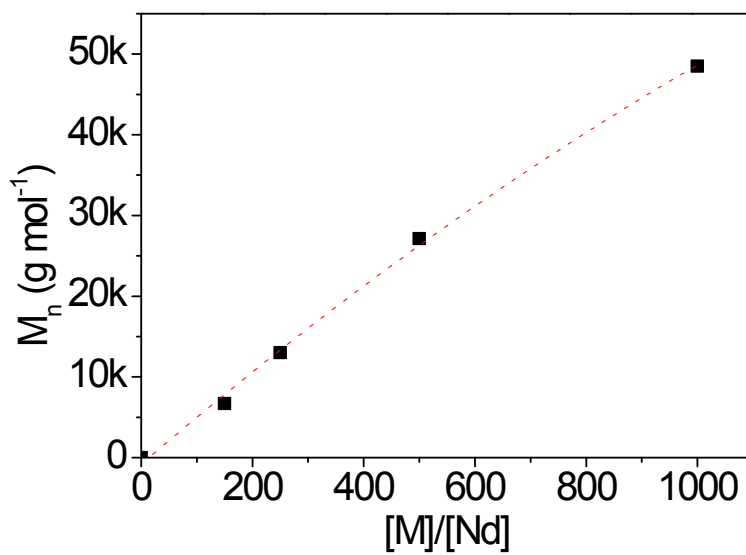


Figure S5. M_n versus $[M]/[Nd]$ ratio. Reaction conditions: room temperature, at the molar ratio of $[M]:[Nd]:[TIBA] = 250:1:30$.

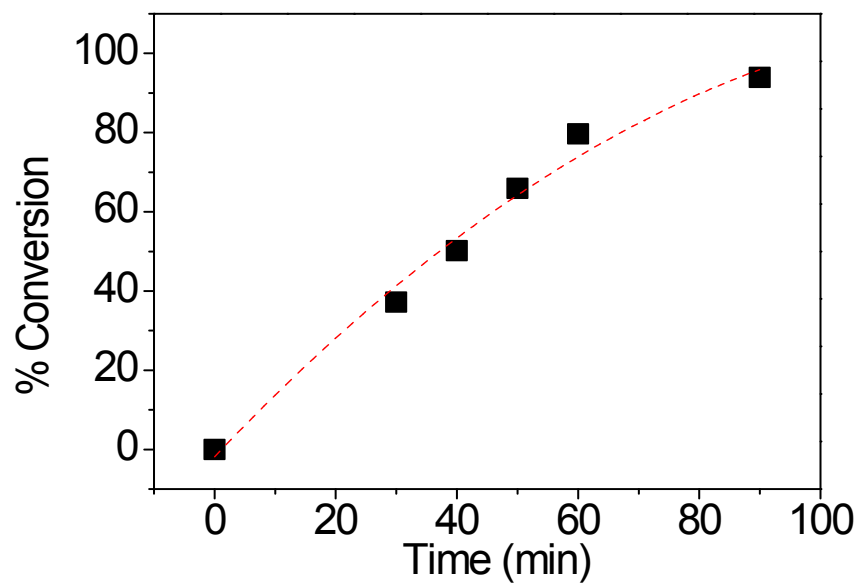


Figure S6. Conversion versus time for the polymerization of β -myrcene at room temperature for the ratio of $[M]:[Nd]:[TIBA] = 250:1:30$.